

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL SEARCH REPORT OR THE DECLARATION

(PCT Rule 44.1)

To: MICHAEL E. WHITHAM MCGUIRE WOODS, LLP 1750 TYSONS BLVD SUITE 1800 MCLEAN VA 22102 <div style="text-align: right; font-weight: bold; font-size: 1.2em;">McGUIRE WOODS LLP</div>

JAN 18 2001

PTO/PC

Date of Mailing <i>(day month year)</i>	
Applicant's or agent's file reference 016401551a	FOR FURTHER ACTION See paragraphs 1 and 4 below
International application No. PCT/US00 26603	International filing date <i>(day month year)</i> 28 SEPTEMBER 2000
Applicant VIRGINIA TECH INTELLECTUAL PROPERTIES, INC.	

1 ☒ The applicant is hereby notified that the international search report has been established and is transmitted herewith.

Filing of amendments and statement under Article 19:
 The applicant is entitled, if he so wishes, to amend the claims of the international application (see Rule 46).

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the international search report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO
 34, chemin des Colombettes
 1211 - Geneva 20, Switzerland
 Facsimile No. (41-22) 740 14 35

For more detailed instructions, see the notes on the accompanying sheet.

2 ☐ The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3 ☐ **With regard to the protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices
☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made

4 **Further action(s):** The applicant is reminded of the following:

Shortly after **18 months** from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in rules 90 *bis* 1 and 90 *bis* 3, respectively, before the completion of the technical preparations for international publication.

Within **19 months** from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within **20 months** from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date, or could not be elected because they are not bound by Chapter II.

Name and mailing address of the ISA/US <small>(name and address of applicant and inventor)</small> P.O. Box 1750, 2201 BLVD, 22201	Authorized Officer ELIZABETH WOOD <div style="text-align: right; font-weight: bold; font-size: 1.2em;">RECORDED</div>
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PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL SEARCH REPORT OR THE DECLARATION

(PCT Rule 44.1)

To: MICHAEL E. WHITHAM MCGUIRE WOODS, LLP 1750 TYSONS BLVD SUITE 1800 MCLEAN VA 22102

Date of Mailing <i>(day month year)</i>	12 JAN 2001
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Applicant's or agent's file reference 01640155a	FOR FURTHER ACTION See paragraphs 1 and 4 below
International application No. PCT/US00 26603	International filing date <i>(day month year)</i> 28 SEPTEMBER 2000
Applicant VIRGINIA TECH INTELLECTUAL PROPERTIES, INC.	

1. <input checked="" type="checkbox"/>	<p>The applicant is hereby notified that the international search report has been established and is transmitted herewith.</p> <p>Filing of amendments and statement under Article 19: The applicant is entitled, if he so wishes, to amend the claims of the international application (see Rule 46).</p> <p>When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the international search report; however, for more details, see the notes on the accompanying sheet.</p> <p>Where? Directly to the International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. (41-22) 740 14 55</p> <p>For more detailed instructions, see the notes on the accompanying sheet.</p>
2. <input type="checkbox"/>	<p>The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.</p>
3. <input type="checkbox"/>	<p>With regard to the protest against payment of (any additional fees) under Rule 46.2, the applicant is notified that</p> <p><input type="checkbox"/> the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.</p> <p><input type="checkbox"/> no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.</p>
4. Further action(s):	<p>The applicant is reminded of the following:</p> <p>Shortly after 18 months from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in rules 90 <i>bis</i> 1 and 90 <i>bis</i> 3, respectively, before the completion of the technical preparations for international publication.</p> <p>Within 19 months from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).</p> <p>Within 20 months from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand, or in a later action within 19 months from the priority date or could not be elected because they are not bound by Chapter II.</p>

Name and mailing address of the ISA's International Patent Institute P.O. Box 1454, 2200 Glen Head, NY 11545	Authorized officer ELIZABETH WOOD DEBORAH TAYLOR <i>(Signature)</i>
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PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 01640155ta	FOR FURTHER ACTION	see Notification of Transmittal of International Search Report (Form PCT/ISA 220) as well as, where applicable, item 5 below.
International application No PCT US00-26603	International filing date (<i>day month year</i>) 28 SEPTEMBER 2000	(Earliest) Priority Date (<i>day month year</i>) 30 SEPTEMBER 1999
Applicant VIRGINIA TECH INTELLECTUAL PROPERTIES, INC.		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1 Basis of the report

a With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item:
☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form
- ☐ filed together with the international application in computer readable form
- ☐ furnished subsequently to this Authority in written form
- ☐ furnished subsequently to this Authority in computer readable form
- ☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the
- ☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2 ☐ **Certain claims were found unsearchable** (See Box I)

3 ☐ **Unity of invention is lacking** (See Box II)

4 With regard to the **title**,

- ☒ the text is approved as submitted by the applicant
- ☐ the text has been established by this Authority to read as follows:

5 With regard to the **abstract**,

- ☒ the text is approved as submitted by the applicant
- ☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6 The figure of the **drawings** to be published with the abstract is: page No. _____

- ☐ as suggested by the applicant
- ☐ because the applicant failed to supply the figure
- ☐ because this figure better characterizes the invention

☒ None of the figures

PCT US 603

According to International Patent Classification (IPC) or to both national classification and IPC

U.S. Please See Extra Sheet.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
Y	US 4,367,137 A (ANTOS ET AL.) 04 JANUARY 1983, SEE PARTICULARLY COLUMN 1, LINES 41-44, COLUMN 4, LINE 54-COLUMN 7, LINE 43 AND COLUMN 14, LINE 27-COLUMN 5, LINE 25.	1-39
X - Y	US 4,454,246 A (FUNG) 12 JUNE 1984, SEE PARTICULARLY COLUMN 3, LINE 16-COLUMN 4, LINE 43.	1-33 ---- 1-33
X - Y	US 4,359,406 A (FUNG) 16 NOVEMBER 1982. SEE PARTICULARLY COLUMN 3, LINE 16-COLUMN 4, LINE 43.	1-33 ---- 1-33

☐ Further documents are listed in the continuation of Box C

☐ See patent family annex

- | | | | |
|---|--|---|---|
| | Special categories of cited documents | | When a document is cited after the international filing date, it prior to date and time of filing with the applicant is referred to as "prior art" and is to be taken into consideration in the inventive step |
| A | document defining the general state of the art which is not considered to be of particular relevance | | |
| B | earliest document published in the international filing date | X | Document of particular relevance: the cited invention cannot be considered to be a prior art; it cannot be considered to involve an inventive step when the document is taken alone |
| C | document which may throw doubt on priority claim, even when cited to establish the prior art, date of invention, or other special reasons as specified | | |
| D | document referring to an invention, even when it refers to other rights | | Document of particular relevance: the cited invention cannot be considered to involve an inventive step when the document is combined with the prior art; other such documents, such as material forming the state of the art, are not taken into account |
| E | document published prior to the international filing date, but not the priority date claimed | X | Document member of the same patent family |

Date of the actual completion of the international course:

01 NOVEMBER 2006

Date of mailing of the international search report

12 JAN 2001

Box 901

ANNALS OF THE ENTOMOLOGICAL SOCIETY OF AMERICA

DEBORA - 740000
PARALELA 500000

INTERNATIONAL SEARCH REPORT

International application No
PCT/US 95/03

A. CLASSIFICATION OF SUBJECT MATTER
IPC (7)

C10G 45 04, B01J 21 02, 21 04, 21 06, 21 08, 21 10, 21 16, 21 18, 27 02, 27 045, 27 08, 27 14, 27 182, 27 185, 27 186,
27 188, 27 19, 27 192, 27 195, 27 198, 27 199

A. CLASSIFICATION OF SUBJECT MATTER
US CL

502 60, 74, 77, 78, 79, 80, 174, 180, 181, 182, 183, 184, 185, 200, 202, 204, 205, 206, 207, 208, 209, 210, 211, 212,
213, 208 143, 216R, 217, 254H

B. FIELDS SEARCHED

Minimum documentation searched

Classification System: US

502 60, 74, 77, 78, 79, 80, 174, 180, 181, 182, 183, 184, 185, 200, 202, 204, 205, 206, 207, 208, 209, 210, 211, 212,
213, 208 143, 216R, 217, 254H

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner
 US Department of Commerce
 United States Patent and Trademark
 Office, PCT
 2011 South Clark Place Room
 CP2/5C24
 Arlington, VA 22202
 ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 30 May 2001 (30.05.01)	
International application No. PCT/US00/26603	Applicant's or agent's file reference 01640155TA
International filing date (day/month/year) 28 September 2000 (28.09.00)	Priority date (day/month/year) 30 September 1999 (30.09.99)
Applicant OYAMA, Shigeo, T.	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:
 14 March 2001 (14.03.01)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO
 34, chemin des Colombettes
 1211 Geneva 20, Switzerland

Authorized officer

Nestor Santesso

Telephone No.: (41-22) 338.83.38

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/26603

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) Please See Extra Sheet
US CL Please See Extra Sheet
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. Please See Extra Sheet.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,367,137 A (ANTOS ET AL.) 04 JANUARY 1983, SEE PARTICULARLY COLUMN 1, LINES 41-44, COLUMN 4, LINE 54-COLUMN 7, LINE 43 AND COLUMN 14, LINE 27-COLUMN 5, LINE 25.	1-39
X - Y	US 4,454,246 A (FUNG) 12 JUNE 1984, SEE PARTICULARLY COLUMN 3, LINE 16-COLUMN 4, LINE 43.	1-33 ---- 1-33
X - Y	US 4,359,406 A (FUNG) 16 NOVEMBER 1982, SEE PARTICULARLY COLUMN 3, LINE 16-COLUMN 4, LINE 43.	1-33 ---- 1-33

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex

* Special categories of cited documents	"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"T" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"F" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

01 NOVEMBER 2000

Date of mailing of the international search report

12 JAN 2001

Name and mailing address of the ISA/US
Harrisville, PA 15005-0001
Box PCT

Authorized officer Telephone No. (703) 308-0661

DEBORAH THOMAS
PARALEGAL SPECIALIST

INTERNATIONAL SEARCH REPORT

International application No
PCT-US00/26603

A. CLASSIFICATION OF SUBJECT MATTER IPC (7)

C10G 45/04, B01J 21/02, 21/04, 21/06, 21/08, 21/10, 21/16, 21/18, 27/02, 27/045, 27/08, 27/14, 27/182, 27/185, 27/186, 27/188, 27/19, 27/192, 27/195, 27/198, 27/199

A. CLASSIFICATION OF SUBJECT MATTER US CL

502/60, 74, 77, 78, 79, 80, 174, 180, 181, 182, 183, 184, 185, 200, 202, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213, 208/143, 216R, 217, 254H

B. FIELDS SEARCHED

Minimum documentation searched

Classification System: U.S.

502/60, 74, 77, 78, 79, 80, 174, 180, 181, 182, 183, 184, 185, 200, 202, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213, 208/143, 216R, 217, 254H

INTERNATIONAL COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

NOTIFICATION OF RECEIPT OF DEMAND BY COMPETENT INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

(PCT Rule 59.3(e) and 61.1(b), first sentence
and Administrative Instructions, Section 601(a))

To:

MICHAEL E. WHITHAM
MCGUIRE WOODS, LLP
1750 TYSONS BLVD
SUITE 1800
MCLEAN VA 22102

Date of mailing
(day/month/year)

13 APR 2001

Applicant's or agent's file reference
01640155TA

IMPORTANT NOTIFICATION

International application No.
PCT/US00/26603

International filing date (day/month/year)
28 SEP 00

Priority date (day/month/year)
30 SEP 99

Applicant

VIRGINIA TECH INTELLECTUAL PROPERTIES, INC.

1. The applicant is hereby **notified** that this International Preliminary Examining Authority considers the following date as the date of receipt of the demand for international preliminary examination of the international application:

14 March 2001 (14-03-01)

2. That date of receipt is:

- ☒ the actual date of receipt of the demand by this Authority (Rule 61.1(b)).
- ☐ the actual date of receipt of the demand on behalf of this Authority (Rule 59.3(e)).
- ☐ the date on which this Authority has, in response to the invitation to correct defects in the demand (Form PCT/IPEA/404), received the required corrections.

3. ☐ **ATTENTION:** That date of receipt is **AFTER** the expiration of 19 months from the priority date. Consequently, the election(s) made in the demand does (do) not have the effect of postponing the entry into the national phase until 30 months from the priority date (or later in some Offices) (Article 39(1)). Therefore, the acts for entry into the national phase must be performed within 20 months from the priority date (or later in some Offices) (Article 22). For details, see the *PCT Applicant's Guide*, Volume II.

- ☐ (If applicable) This notification confirms the information given by telephone, facsimile transmission or in person on:

4. Only where paragraph 3 applies, a copy of this notification has been sent to the International Bureau.

WHITHAM CURTIS & WHITHAM

RECEIVED
16 APR 2001
PCT/US00/26603

Name and mailing address of the IPEA US
Assistant Commissioner for Patents
Box PCT
Washington, D.C. 20231
Facsimile No.

Attn: IPEA US

Authorized Officer

Telephone No.

301-228-6454

PATENT COOPERATION TREATY

PCT

REC'D 18 APR 2002

W/ED

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 01640155TA	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT IPEA 416)	
International application No. PCT/US00/26603	International filing date (day/month/year) 28 September 2000 (28.09.2000)	Priority date (day/month/year) 30 September 1999 (30.09.1999)
International Patent Classification (IPC) or national classification and IPC IPC(7): C10G 45/04; B01J 21/02, 21/04, 21/06, 21/08, 21/10, 21/16, 21/18, 27/02, 27/045, 27/08, 27/14, 27/18 and US Cl.: 502/60, 74, 77, 78, 79, 80, 174, 180, 181, 182, 183, 184, 185, 200, 202, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213; 208/143, 216R, 217, 254h		
Applicant VIRGINIA TECH INTELLECTUAL PROPERTIES, INC.		
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of <u>4</u> sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of <u>0</u> sheets.</p>		
<p>3. This report contains indications relating to the following items:</p> <p>I <input checked="" type="checkbox"/> Basis of the report</p> <p>II <input type="checkbox"/> Priority</p> <p>III <input type="checkbox"/> Non-establishment of report with regard to novelty, inventive step and industrial applicability</p> <p>IV <input type="checkbox"/> Lack of unity of invention</p> <p>V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p>VI <input type="checkbox"/> Certain documents cited</p> <p>VII <input type="checkbox"/> Certain defects in the international application</p> <p>VIII <input checked="" type="checkbox"/> Certain observations on the international application</p>		
Date of submission of the demand 14 March 2001 (14.03.2001)	Date of completion of this report 11 March 2002 (11.03.2002)	
Name and mailing address of the IPEA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703)305-3230	Authorized officer Elizabeth Wood Telephone No. 703-308-0661	

Form PCT IPEA/409 (cover sheet) (July 1998)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No

PCT/US00/26603

I. Basis of the report

1. With regard to the **elements** of the international application: *

- ☒ the international application as originally filed.
- ☒ the description:
pages 1-22 as originally filed
pages NONE, filed with the demand
pages NONE, filed with the letter of _____
- ☒ the claims:
pages 23-30 as originally filed
pages NONE, as amended (together with any statement) under Article 19
pages NONE, filed with the demand
pages NONE, filed with the letter of _____
- ☒ the drawings
pages 1-6 as originally filed
pages NONE, filed with the demand
pages NONE, filed with the letter of _____
- ☐ the sequence listing part of the description:
pages NONE, as originally filed
pages NONE, filed with the demand
pages NONE, filed with the letter of _____

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
These elements were available or furnished to this Authority in the following language _____ which is:

- ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in printed form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

4. ☒ The amendments have resulted in the cancellation of

- ☐ the description, pages NONE
- ☐ the claims, Nos. NONE
- ☐ the drawings, sheets/~~fig~~ NONE

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)). **

* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

** Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No
PCT/US00/26603**V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability: citations and explanations supporting such statement****1. STATEMENT**

Novelty (N)	Claims <u>14-28 AND 34-39</u>	YES
	Claims <u>1-13 AND 29-33</u>	NO
Inventive Step (IS)	Claims <u>NONE</u>	YES
	Claims <u>1-39</u>	NO
Industrial Applicability (IA)	Claims <u>1-39</u>	YES
	Claims <u>NONE</u>	NO

2. CITATIONS AND EXPLANATIONS

Claim 1-39 lack an inventive step under PCT Article 33(3) as being obvious over Antos et al.

The instant claims are directed to a catalyst composition comprising a supported metal phosphide composition, methods for making this composition and the use thereof in a hydrotreating process.

Antos et al. disclose catalytic composites having utility in desulfurization processes. The composites comprise supported phosphorus components that are taught to be a phosphide with a cobalt component, substantially as claimed herein by applicant.

Antos et al. differ from the subject invention in that the scope of Antos et al. and the instant claims is different. Antos et al. require a number of other components not claimed by applicant. However, the open claim language of "comprising" does not exclude such components.

Claims 1-13 and 29-33 lack novelty under PCT Article 33(2) as being anticipated by or alternatively, lack an inventive step under PCT Article 33(3) as being obvious over either Fung '246 or Fung '406.

The Fung references disclose supported binary metal phosphorus compounds that anticipate the herein claimed composition. Alternatively, the Fung references can be considered to differ in scope from the instant invention in that Fung discloses only group VIII metal phosphides whereas the instant claims embrace some group VIII metals as well as metals from other groups. The instant claims would have been obvious, however, because the skilled artisan is more than capable of selecting one from a specifically disclosed group of metals.

Claims 1-39 meet the criteria of PCT Article 33(4) because the claimed catalysts have utility in the field of hydrocarbon conversion.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No

PCT/US00 26603

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the questions whether the claims are fully supported by the description, are made:

Claims 1-39 are objected to under PCT Rule 66.2(a)(v) as lacking clarity under PCT Article 6 because the claims are indefinite for the following reasons:

The claims are indefinite in the use of the terminology "high surface area" because this is relative terminology with no point of reference.

Claims 20-23 do not appear to further limit the claimed process and or are inherent thereto. Since the independent claim recites contact with the catalyst, the catalyst will inherently carry out the claimed steps.

Claim 28 is improper in that it recites the "catalyst" of claim 14 when claim 14 is drawn to a method.

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
5 April 2001 (05.04.2001)

PCT

(10) International Publication Number
WO 01/23501 A1

(51) International Patent Classification: **C10G 45/04**,
B01J 21/02, 21/04, 21/06, 21/08, 21/10, 21/16, 21/18,
27/02, 27/045, 27/08, 27/14, 27/182, 27/185, 27/186,
27/188, 27/19, 27/192, 27/195, 27/198, 27/199

(21) International Application Number: PCT/US00/26603

(22) International Filing Date:
28 September 2000 (28.09.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/156,701 30 September 1999 (30.09.1999) US

(71) Applicant (for all designated States except US): **VIRGINIA TECH INTELLECTUAL PROPERTIES, INC.**
[US/US]; 1872 Pratt Drive, Suite 1625, Blacksburg, VA
24060 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **OYAMA, Shigeo, T.**
[US/US]; Virginia Polytechnic Institute and State University,
133 Randolph Hall, Blacksburg, VA 24060 (US).

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(54) Title: NOVEL TRANSITION METAL PHOSPHIDE CATALYSTS

(57) Abstract: There is provided a transition metal phosphide catalyst that is active for hydrotreating hydrocarbon feedstocks. The catalyst comprises a transition metal phosphide complex supported on a high surface area support. The high surface area support may be selected from the group consisting of carbon, silica, alumina, titania, thoria, magnesia, zirconia, kaolin, bentonite, kieselguhr, zeolites and combination thereof. The transition metal phosphide complex may include a mixed metal phosphide complex. The catalyst comprises a metal phosphide complex having the formula MP_x , where M is selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, and where x is between about 0.1 and about 10; and an oxide support, where the metal phosphide complex is dispersed on the high surface area support. Further, the catalyst comprises a metal phosphide catalyst comprising a metal phosphide complex having the formula $A_xB_yP_z$, where A and B are each selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, where the sum of a and b is 1, the ratio of a to b is between about 0.01 and about 100, and y is between about 0.1 and about 10; and an oxide support, where the metal phosphide complex is dispersed on the high surface area support. Further, there is provided a method for hydrotreating a hydrocarbon feed using a transition metal phosphide catalyst. A method for hydrodesulfurization, including deep hydrodesulfurization, using the above catalysts is also described.

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NOVEL TRANSITION METAL PHOSPHIDE CATALYSTS

This application is based on U.S. Provisional Application No. 60/156,701 filed September 30, 1999 herein incorporated by reference in its entirety.

Background of the Invention*Field of the Invention*

This invention pertains to a catalyst composition and a method for hydrotreating hydrocarbon feedstocks, and more particularly to hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrogenation (HYD).

Background Description

Phosphorus has been used in combination with transition metals on supports for use in hydrotreating hydrocarbon feedstocks. In these cases, the phosphorus is in the form of an oxide (phosphate) usually incorporated as an additive. From the literature it is understood that the phosphorus can have multiple roles. For example, it can stabilize the surface area of the support, prevent the formation of compounds such as cobalt or nickel aluminate, alter acid-base properties, or aid in the dispersion of the metals in the catalyst.

Several references have utilized phosphorus as an oxide component. For example, U.S. Patent Number 4,600,703 describes a catalyst composed of Mo, Ni, and phosphorus oxide deposited on an alumina support and calcined at 450-650 °C. U.S. Patent Number 4,520,128 describes a catalyst composed of a group 6 metal, a group 8 metal, and phosphorus oxide on an alumina support and calcined at 400-600 °C. U.S. Patent Number 4,687,568 describes a catalyst consisting of Ni sulfide supported on a Zr compound to which is added a compound containing P and O. U.S. Patent Number 4,707,246 describes a catalyst containing either Mo, zinc titanate, either Ni or Co

supported on alumina to which is added a compound containing P and O. In U.S. Patent Number 4,392,985 to a catalyst composed of Mo promoted with Co is added P in the form of orthophosphoric acid, and then calcined at a temperature of at least 750 °F (400 °C). In U.S. Patent Number 4,388,222 to a catalyst composed of Mo promoted with Ni or Co is added P in the form of phosphoric acid, and is then calcined. In U.S. Patent Number 4,632,914 Mo, W, Co and Ni are supported on bauxite and to this is added orthophosphoric acid followed by calcination between 300-600 °C. U.S. Patent Number 4,588,706 and U.S. Patent Number 4,689,314 describe a catalyst constituted of a group 6 metal, a group 8 metal and P in the form of phosphoric acid which is calcined at 400-550 °C. WO 9,708,273A1, U.S. Patent Number 4,941,964, and U.S. Patent Number 5,322,616 describe a catalyst comprising an alumina support, a group 8 metal oxide, a group 6 metal oxide, and phosphorus oxide. In U.S. Patent Number 4,743,574 the phosphorus is added to the alumina support to form an aluminum phosphate, and on this are added Co and Mo oxides. U.S. Patent Number 3,755,148, U.S. Patent Number 3,755,150, and U.S. Patent Number 3,755,196 describe supported catalysts containing Mo, Ni or Co with P added as orthophosphoric acid.

Several references describe catalyst preparation conditions where the phosphorus is transformed to an oxide. For example, in U.S. Patent Number 4,446,248 a catalyst containing Mo, Ni, and P on alumina is calcined between 975-1025 °F (525 -550 °C). In U.S. Patent Number 4,003,828 a catalyst containing Mo or W and Co or Ni is prepared on a support obtained by cogellation of alumina and phosphorus oxide. U.S. Patent Number 5,021,385 describes a catalyst prepared by adding Mo and Ni and optionally P to a hydrogel of Ti and Zr and calcining between 325-450 °C. U.S. Patent Number

4,716,141 and U.S. Patent Number 4,738,945 describe a catalyst prepared by adding Ni and either Mo or W with P to an alumina obtained by precipitation and calcining between 300-900 °C. U.S. Patent Number 4,717,705 describes a catalyst prepared by adding Co and either Mo or W with P to an alumina obtained by precipitation and calcining between 300-900 °C. After the calcination step the metals are converted to sulfides by a separate sulfidation step for example at 250-330 °C as described in U.S. Patent Number 4,689,314 or by exposure to a feed containing sulfur. In no case are phosphides formed at the conditions of preparation.

In the cases described above, the phosphorous component in standard catalysts is found in oxidized form, essentially a phosphate compound. This oxidation occurs as a result of calcination (high temperature treatment in air or oxygen). The presence of phosphate in the standard catalysts is well established by nuclear magnetic resonance (NMR) and x-ray photoelectron spectroscopy (XPS) studies. One example, is U.S. Patent Number 5,462,651 which reports the NMR chemical shift for phosphate as occurring between -5 and -30 ppm. In phosphides the NMR chemical shift occurs between +30 and +300 ppm.

Summary of the Invention

The present invention is directed to a catalyst where the phosphorous component is in reduced form, in the form of a phosphide highly dispersed on a high surface area support. The formation of the phosphide on the support is a result of high temperature reduction during preparation of the catalyst. Catalysts prepared in accordance with the present invention produce a highly dispersed catalyst in which the surface area of the metal component is enhanced.

An object of this invention is to provide a transition metal phosphide catalyst highly dispersed on a high surface area support. Another object of the present invention is to provide a transition metal phosphide catalyst for hydrotreating hydrocarbon feedstocks. Further, an object of the present invention is to provide a catalyst material
5 that that is easy to prepare through the reduction of phosphate, and that is easy to regenerate through reduction or by oxidation followed by reduction.

The present invention includes a catalyst comprising a metal phosphide complex having the formula MP_x , where M is selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, and where x ranges from about 0.1 to about 10; and a high
10 surface area support, where the metal phosphide complex is dispersed on the high surface area support. Further, in a preferred embodiment, x may range from about 0.5 and about 3.

The high surface area support may be selected from the group consisting of carbon, silica, alumina, titania, thoria, magnesia, zirconia, kaolin, bentonite, kieselguhr,
15 zeolites, and combinations thereof. The metal phosphide complex may be supported on the high surface area support in the range from about 1 to about 40% by weight of complex to support and preferably in the range from about 10 to about 30% by weight of complex to support.

The invention further includes a metal phosphide catalyst comprising a metal
20 phosphide complex having the formula $A_aB_bP_y$, where A and B are each selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, where the sum of a and b is 1, the ratio of a to b is between about 0.01 and about 100, and y is between about 0.1 and about 10. The ratio of a to b may range from about 0.1 to about 10. Further, the

ratio of a to b may preferably range from about 0.2 and 5. Further, y may preferably range from about 0.5 and about 3. The metal phosphide complex is dispersed on the high surface area support.

The present invention more generally includes a metal catalyst comprising at least one metal selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, wherein at least a portion of the one metal is in the form of a phosphide; and a high surface area support wherein the at least one metal and said phosphide are highly dispersed on said high surface area support.

The catalysts of the present invention may also include a promoter selected from the group consisting of the alkali metals, alkaline earth metals, platinum group metals, rhenium, copper, halides, boron, carbon, nitrogen, aluminum, sulfur, gallium, germanium, arsenic, tin, antimony, bismuth, selenium and tellurium.

Further, the invention includes a method for hydrotreating a hydrocarbon feed comprising the step of exposing the hydrocarbon feed to a catalyst in an atmosphere containing hydrogen, where the catalyst comprises at least one metal selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, wherein at least a portion of the one metal is in the form of a phosphide; and a high surface area support wherein the at least one metal and said phosphide are dispersed on said high surface area support. The phosphide may have the formula MP_x , where M is selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, and where x ranges from about 0.1 and about 10. Further, x may preferably range from about 0.5 and about 3. The phosphide may have the formula $A_aB_bP_y$, where A and B are each selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, wherein the sum of a and b is 1.

the ratio of a to b ranges from about 0.01 to about 100, and y ranges from about 0.1 and about 10. The ratio of a to b may preferably range from about 0.1 to about 10. Further, the ratio of a to b may preferably range from about 0.2 to 5, and y may preferably range from about 0.5 to about 3.

5 The invention includes a method of hydrotreating a hydrocarbon feed where the step of exposing the hydrocarbon feed to a catalyst is sufficient to remove nitrogen from the hydrocarbon feed.

 The invention includes a method of hydrotreating a hydrocarbon feed where the step of exposing the hydrocarbon feed to a catalyst is sufficient to remove oxygen from
10 the hydrocarbon feed.

 The invention includes a method of hydrotreating a hydrocarbon feed where the step of exposing the hydrocarbon feed to a catalyst is sufficient to hydrogenate an unsaturated organic compound in the hydrocarbon feed.

 The invention includes a method of hydrotreating a hydrocarbon feed where the
15 step of exposing the hydrocarbon feed to a catalyst is sufficient to hydroisomerize an organic compound in the hydrocarbon feed.

 The method of the present invention may include a hydrocarbon feed selected from the group consisting of middle distillates, kero, naptha, gas oil obtained by catalytic cracking, gas oil obtained by thermal cracking, straight-run gas oil, coker gas oil, vacuum
20 gas oils, heavy gas oils, coal liquids, feeds extracted from tar sands, and feeds extracted from shale.

 Further, the method may include the step of processing the hydrocarbon feed in the presence of the catalyst at a temperature ranging from about 250 to about 450 °C.

pressure ranging from about 5 to about 250 bar, space velocities ranging from about 0.1 to about 10 hr⁻¹, and H₂ feed ratios ranging from about 1000 to about 15000 scf/barrel.

Further, the invention includes a method for hydrodesulfurizing a hydrocarbon feed wherein the feed contains sulfur compounds that include sterically hindered, alkyl substituted heteroaromatic condensed rings. The hydrodesulfurization process consists of exposing the hydrocarbon feed to a catalyst, wherein the catalyst comprises at least one metal selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, wherein at least a portion of the one metal is in the form of a phosphide; and a high surface area support wherein the at least one metal and said phosphide are dispersed on said high surface area support. The phosphide may have the formula MP_x, where M is selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, and where x ranges from about 0.1 and about 10. Further, x may preferably range from about 0.5 and about 3. The phosphide may have the formula A_aB_bP_y, where A and B are each selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, wherein the sum of a and b is 1, the ratio of a to b ranges from about 0.01 to about 100, and y ranges from about 0.1 and about 10. The ratio of a to b may preferably range from about 0.1 to about 10. Further, the ratio of a to b may preferably range from about 0.2 to 5, and y may preferably range from about 0.5 to about 3.

Brief Description of the Drawings

- Figure 1 shows X-ray diffraction patterns of fresh and spent 23 wt% MoP/Al₂O₃.
Figure 2 shows X-ray diffraction patterns of fresh and spent MoP/SiO₂.
Figure 3 shows X-ray diffraction patterns of fresh and spent WP/SiO₂.
Figure 4 shows X-ray diffraction patterns of fresh and spent 8.6 wt% Ni₂P/SiO₂.

Figure 5 shows X-ray diffraction patterns of fresh and spent CoP/SiO₂.

Figure 6 shows X-ray diffraction patterns of fresh and spent Fe₂P/SiO₂.

Figure 7 shows X-ray diffraction patterns of NiMoP₂.

Figure 8 shows the reactivity of phosphides in hydroprocessing.

5 Figure 9 shows the X-ray diffraction patterns of WP before and after reaction.

Figure 10 shows a comparison of conversion of 4,6-dimethyldibenzothiophene.

Detail Description of the Invention

The present invention is directed to a catalyst composition and a method for hydrotreating hydrocarbon feedstocks, more particularly hydrodesulfurization (HDS),
10 hydrodenitrogenation (HDN), hydrodeoxygenation, hydroisomerization, and hydrogenation (HYD). The invention further relates to processes for the preparation and use of a catalyst composition.

In general, hydrotreating refers to the removal of sulfur (HDS) and nitrogen (HDN) from hydrocarbon feedstocks. The removal of these components is important for
15 producing clean burning fuels. In addition, it is essential to remove these elements, since the catalysts used in subsequent processing, like cracking, hydrocracking, and reforming, are poisoned by the sulfur and nitrogen.

The present invention provides new types of catalysts for hydrotreating hydrocarbon feedstocks. The catalysts are supported transition metal phosphides, a class
20 of material in which the phosphorus forms a chemical compound with the metal component. The metal source can be quite diverse and includes the ammonium salts, chlorides, nitrates, hydroxides, heteropoly compounds and other species. The transition metals that may be used in the catalyst of the present invention includes, but is not

limited to, Mo, W, Fe, Co, Ni, V, Nb, Cr, Mn, Ta, and other suitable transition metals. The catalyst may be prepared according to the formula MP_x , where M is a metal and x may range from about 0.1 to about 10. Preferably x ranges from about 0.5 to about 3.

The metals may be combined in various ratios to form multimetallic phosphides according to the formula $A_aB_bP_y$ where A and B are metals and where the sum of a and b is 1, the ratio of a to b ranges from about 0.01 to about 100, and y ranges from about 0.1 to about 10. Preferably the ratio of a to b ranges from about 0.1 to about 10 and most preferably the ratio of a to b ranges from about 0.2 to 5. Further, y preferably ranges from about 0.5 to about 3. Mixed metal compositions can give rise to diverse substances with potentially very unique properties such as activity, or selectivity for the hydrotreating reactions. Some of the mixed metal composition includes $Mo_aCo_bP_y$, $Mo_aNb_bP_y$, $W_aNi_bP_y$, and the like. It will be evident to those skilled in the art that a wide variety of multimetallic phosphides can be prepared where the catalyst contains three or more metal elements.

The phosphorus source can be similarly diverse, and includes phosphoric acid, phosphorous acid, and the various ammonium hydrogen phosphates. The relative amounts of phosphorus (P) and metal (M) are given by molar percentages of 50 to 300 mol% which correspond to stoichiometries of $MP_{0.5}$ to MP_3 .

The catalysts are in supported form, where the active metal phosphide is present on the support as either small particles or as a surface phase. The metal phosphide may be present on the support as particles ranging from 1nm to about 10 μ m in size. Dispersing the metal phosphide on the high surface area support increases the surface area of the metal phosphide compared to the bulk form. The phosphides are deposited on

a high surface area support in order to disperse and utilize the phosphide component more effectively. The metal phosphide is loaded on the support in the range from about 1 to about 40% by weight metal phosphide to support. Preferably, the metal phosphide is loaded on the support in the range of about 10 to about 30% by weight metal phosphide to support. As used herein, "high surface area support" is a support preferably having a surface area of at least about 50 m²/g. Most preferably, the support has a surface area of at least about 100 m²/g (BET method) and a pore volume in the range of 0.25-1.3 cm³/g (mercury penetration method). The supports include, but are not limited to, substances like silica, alumina, titania, thoria, magnesia, zirconia, kaolin, bentonite, kieselguhr, zeolites, carbon, other high surface area supports, and combinations thereof. Preference is given to alumina or silica or combinations thereof.

A preferred method of preparation for the catalysts involves the reduction of precursor phosphates in a stream of hydrogen. One suitable method of preparing the catalyst is impregnating the supports with solutions of the metal and phosphorus components, and optionally drying at 25-200 °C and calcining in air or oxygen in the range of 350-750 °C so as to intimately mix the components. The resulting material is then reduced in a hydrogen stream at temperatures between 300 °C and 1000 °C, preferably 400-700 °C. Following reduction the catalyst can be used as such by exposure to the desired feed. If the catalyst needs to be transported to another site it can be passivated in a stream of oxygen in an inert gas which can start at low concentrations (0.1%) and gradually go up (21%). The catalyst treated in this manner can undergo re-reduction in hydrogen at temperatures from 300-700 °C, or be activated by direct contact

with the feed. The catalyst is typically formed as spheres or extrudates, which include symmetrical and asymmetrical polylobed particles.

It will be clear to those skilled in the art that there can be a wide number of variations on this method. It should be possible to apply a plurality of impregnating steps, the impregnating solutions containing one or more of the component precursors, or a portion thereof. Instead of impregnating techniques other methods like dipping methods, or spraying methods can be used to deposit the active components on the support. Similarly, there can be a multitude of variations on the mode and order of drying, calcining, and shaping of the catalyst.

It should also be clear to those skilled in the art that there can be a large number of promoters added to the catalysts to enhance their activity, selectivity or stability. These include, but are not limited to, the alkali metals, alkaline earth metals, platinum group metals, rhenium, copper, halides, as well as main group elements like boron, carbon, nitrogen, aluminum, sulfur, gallium germanium, arsenic, tin, antimony, bismuth, selenium and tellurium.

The catalysts of the present invention have high activity for hydrosulfurization and hydrodenitrogenation of hydrocarbon feedstocks. The activity, based on an equivalent surface area, is higher than that of a commercial catalyst studied at the same conditions. The conditions are typical of industrial processes and involve high temperature and pressure. The catalyst of the present invention show high stability with no deactivation over a hundred hours of reaction time.

The present catalysts can be used in the hydrotreating of a wide variety of feeds. These include, but are not limited to middle distillates, kero, naptha, gas oil obtained by

catalytic cracking, gas oil obtained by thermal cracking, straight-run gas oil, coker gas oil, vacuum gas oils, heavy gas oils, coal liquids, and feeds extracted from tar sands or shale. The conventional process conditions are temperatures in the range of 250-450 °C, pressures in the range of 5-250 bar, space velocities in the range of 0.1-10 hr⁻¹, and H₂/oil ratios in the range of 1000-15000 scf barrel.

Various aspects of the present invention are illustrated in the following examples. The examples are provided for illustration purposes and should not be construed as limiting the scope of the present invention.

Example 1

Preparation and characterization of MoP/Al₂O₃

Ammonium paramolybdate (Aldrich, 95%) and ammonium phosphate (Aldrich, 99%) were dissolved in distilled water and the solution was used to impregnate a γ -Al₂O₃ support (Degussa, Aluminoxid C) to the point of incipient wetness. The moist paste was calcined in air at 773 K for 6 hours, ground with a mortar and pestle, pressed to 4000 psi, broken, and sieved to particles between 650 and 1180 μ m for use. The pelletized precursors were placed in quartz u-tube reactors, and heated with linear temperature ramps (heating rate = 5 K min⁻¹) in flowing hydrogen (Airco, 99.999%) to reduce the metal phosphate to metal phosphide. The hydrogen flow was set at 975 cm³ min⁻¹ per gram of precursor loaded and the final temperature was 850 °C. After reduction the product was cooled to room temperature under helium and passivated progressively with 0.1% O₂/He and then 0.5% O₂/He, then exposed to air in the sample tube for 24 hours. The samples were characterized by CO uptake measurements after reduction in hydrogen for 2 hours at 350 °C. The physical characteristics are shown in Table I. X-ray

diffraction spectra were collected using a Scintag XDS-2000 diffractometer. The physical properties and x-ray diffraction pattern of the material are shown in Figure 1. Comparison of the XRD patterns of the supported catalysts to a bulk MoP reference from the powder diffraction files (pdf 24-771) shows the presence of supported MoP.

5 Table I. Physical characteristics of MoP/Al₂O₃ catalysts

Sample [†]	Physical Characteristics	
	Surface Area m ² g ⁻¹	CO Uptake μmol g ⁻¹
Al ₂ O ₃ blank	90.6	-
6.8 wt%	74.8	20.0
12.8 wt%	71.4	30.6
12.8 wt%*	73.7	29.4
22.7 wt%	59.6	28.8
38.9 wt%	48.8	26.3

† Reduced to 850 °C (β = 5 K min⁻¹, s.v. = 1000 sccm g⁻¹) for 2 hours

* Reduced to 750 °C (β = 5 K min⁻¹, s.v. = 1000 sccm g⁻¹) for 2 hours

Example 2

Preparation and characterization of MoP/SiO₂

10 The catalyst was prepared in the same manner as in example 1, except that the support used was SiO₂ (Cabosil L90). The physical properties are listed in Table II and

the x-ray diffraction patterns of the material are shown in Figure 2. The XRD patterns of the supported catalysts show a large broad feature at 20° , but otherwise the pattern corresponds to that of MoP as shown by the reference.

Table II. Physical characteristics of MoP/SiO₂ catalysts

Sample	Physical Characteristics	
	Surface Area m ² g ⁻¹	CO Uptake μ mol g ⁻¹
SiO ₂ blank	91	-
MoP/SiO ₂	50	50

5

Example 3

Preparation and characterization of WP/SiO₂

The catalyst was prepared in the same manner as in example 1, except that the precursor used was ammonium paratungstate (Aldrich, 95%), and the support used was SiO₂ (Cabosil L90). The physical properties are shown in Table III below and the x-ray diffraction pattern of the material is shown in Figure 3. The XRD pattern of the supported catalysts show a large broad feature at 20° , but otherwise the pattern corresponds to that of WP as shown by the reference spectrum from the powder diffraction files (pdf 29-1364).

10

Table III. Physical characteristics of WP/SiO₂ catalysts

Sample	Physical Characteristics	
	Surface Area m ² g ⁻¹	CO Uptake μ mol g ⁻¹

SiO ₂ blank	91	-
6.8 wt% WP SiO ₂	62	19

In situ phosphorus 31 solid-state NMR confirms that a highly dispersed phase WP is formed on an inert SiO₂ support, with the same signal (chemical shift of 252 ppm, and high anisotropy) as a bulk sample. This indicates that the supported samples have the same structure as the bulk, but a substantially higher surface area.

5

Example 4

Preparation and characterization of Ni₂P/SiO₂

To a solution of ammonium phosphate (Aldrich, 99%) in distilled water was added nickel nitrate (Aesar, 19.8% Ni). An excess of phosphorus was used, so that molar ratios of Ni:P of 1:1 and 1:2 were used, corresponding to weight percents of 9.4 and 12.2%. A precipitate formed which was dissolved by the addition of a few drops of nitric acid (Fisher, 69.4% assay). Water was added to form enough solution to carryout an incipient wetness impregnation of a silica (Cabosil L90) support. The solid was dried at 120 °C for 3 hours and calcined at 500 °C for 6 hours. It was reduced in a temperature programmed manner with a heating rate of 1 K min⁻¹ to 577 °C. The physical properties are listed in Table IV below and the x-ray diffraction pattern of the material is shown in Figure 4.

15

Table IV. Physical characteristics of Ni₂P/SiO₂ catalysts

Sample	Physical Characteristics	
	Surface Area m ² g ⁻¹	CO Uptake μmol g ⁻¹

9.4 wt% Ni ₂ P/SiO ₂ †	118	15
12.2 wt% Ni ₂ P/SiO ₂ *	132	29

† Ni:P = 1:1 * Ni:P = 1:2

Example 5

Preparation and characterization of CoP/SiO₂

The catalyst was prepared in the same manner as in example 4, except that the precursor was cobalt nitrate (Aldrich, 99%) and no nitric acid was needed to form a solution. Equimolar quantities of Co and P were used. The final temperature reduction was 690 °C. The physical properties are listed in Table V below and the x-ray diffraction pattern of the material is shown in Figure 5.

Table V. Physical characteristics of CoP/SiO₂ catalysts

Sample	Physical Characteristics	
	Surface Area m ² g ⁻¹	CO Uptake μmol g ⁻¹
CoP/SiO ₂	134	16

Example 6

Preparation and characterization of Fe₂P/SiO₂

The catalyst was prepared in the same manner as in example 4, except that the precursor was iron nitrate (Aldrich, 99.9%) and no nitric acid was needed to form a solution. Equimolar quantities of Fe and P were used. The final temperature of reduction

was 730 °C. The physical properties are listed in Table VI below and the x-ray diffraction pattern of the material is shown in Figure 6.

Table VI. Physical characteristics of Fe₂P/SiO₂ catalysts

Sample	Physical Characteristics	
	Surface Area m ² g ⁻¹	CO Uptake μmol g ⁻¹
Fe ₂ P/SiO ₂	153	16

Example 7

5 Preparation and characterization of NiMoP₂/SiO₂

A solution of ammonium paramolybdate (Aldrich, 95%) and ammonium phosphate (Aldrich, 99%) in distilled water was prepared. To this solution was added nickel nitrate (Aesar, 19.8% Ni) in an amount to form a stoichiometry of Ni:Mo:P = 1:1:3. A precipitate formed, but could be made to dissolve by the addition of a few drops
10 of nitric acid. Water was added to form enough solution to carry out an incipient wetness impregnation of a silica support (Cabosil, L90). The resulting solid was dried at 120 °C and calcined at 500 °C for 6 hours. It was reduced in a temperature programmed manner with a heating rate of 1 K min⁻¹ to 620 °C. The physical properties are listed in Table VII below and the x-ray diffraction pattern of the material is shown in Figure 7.

15 Table VII. Physical characteristics of NiMoP₂/SiO₂ catalysts

Sample	Physical Characteristics	
	Surface Area m ² g ⁻¹	CO Uptake μmol g ⁻¹

NiMoP ₂	-	-
NiMoP ₂ /SiO ₂	153	55

Example 8

Hydrotreating activities of MoP/Al₂O₃ catalysts

Hydrotreating of a model petroleum liquid consisting of quinoline (Aldrich, 99%), benzofuran (Aldrich, 99%), dibenzothiophene (Aldrich, 99%), tetralin (Aldrich, 99%), and tetradecane (Fisher, 99%), was carried out in a pressurized three-phase trickle bed reactor. Analysis was performed with a gas chromatograph (Hewlett Packard, 5890A) on liquid product collected at 2-3 hours intervals. An amount of catalyst corresponding to 70 μmol of CO sites was loaded to the reactor. To start the reaction catalyst were pretreated in hydrogen at 623 K and 1 atm for 2 hours. The conditions were set to 3.1Mpa (450 psig), a hydrogen flow rate at 150 $\text{cm}^3 \text{min}^{-1}$ and a liquid feed rate of 5 $\text{cm}^3 \text{min}^{-1}$. The results of the catalytic tests are listed in Table VIII below.

Table VIII. Hydrotreating activities of MoP/Al₂O₃ catalysts

Sample †	Hydrotreating Performance		
	HDN %	HYD %	HDS %
6.8 wt%	54	31	51
12.8 wt%	52	33	57
12.8 wt%*	62	29	57
22.7 wt%	58	28	53
38.9 wt%	54	33	44

† Reduced to 1123 °C ($\beta = 5 \text{ K min}^{-1}$, s.v. = 1000 sccm g^{-1}) for 2 hours

* Reduced to 1023 °C ($\beta = 5 \text{ K min}^{-1}$, s.v. = 1000 sccm g^{-1}) for 2 hours

Example 9

Hydrotreating activities of MoP/SiO₂, WP/SiO₂, Ni₂P/SiO₂, CoP/SiO₂, Fe₂P/SiO₂, and

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NiMoP₂/SiO₂ catalysts

The catalysts MoP/SiO₂, WP/SiO₂, Ni₂P/SiO₂, CoP/SiO₂, Fe₂P/SiO₂, and NiMoP₂/SiO₂ were tested as in example 8. The results are listed in Table IX. In both the difficult HDN reaction and the HDS reaction, the phosphides had substantially higher activity than a reference MoS₂/SiO₂ catalyst.

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A concern with the use of any catalyst is its stability in the reaction medium. The phosphides were tested for 100 hours and did not display deactivation. Analysis of the products by XRD after reaction revealed that there was no change in bulk crystal structure (Figures 1-6). Furthermore, XPS revealed that only about 2 mol% of sulfur accumulated on the surface of the catalysts after reaction for 100 hours. These results

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demonstrate that the catalysts are completely stable in a sulfur environment.

Table IX. Hydrotreating activities of phosphide catalysts

Sample	Hydrotreating Performance		
	HDN %	HYD %	HDS %
MoP/SiO ₂	31	45	20
Wp/SiO ₂	40	46	13
Ni ₂ P/SiO ₂ †	14	38	90
Ni ₂ P/SiO ₂ *	80	19	98
CoP/SiO ₂	30	52	30

Fe ₂ P/SiO ₂	2	11	3
NiMoP ₂ /SiO ₂	34	45	25
MoS ₂ /SiO ₂	11	45	31

† Ni:P = 1:1 * Ni:P = 1:2

Example 10

The catalysts were tested for HDN, HDS, and hydrogenation (HYD) activity in a trickle bed reactor operated at 643 K (370 °C) and 3.1 Mpa (450 psig). These are standard conditions typically used in an industrial hydroprocessing unit. The reactant feed consisted of quinoline (2000 ppm N), dibenzothiophene (3000 ppm S), tetralin (20 wt.%), and tetradecane (balance). An amount corresponding to 30 m² of catalyst was loaded in the reactor.

The results of the phosphide catalyst compared to NiMoS/Al₂O₃ are shown in Figure 8. In the difficult HDN reaction, tungsten phosphide had substantially higher activity than the commercial NiMo catalyst (58% vs 38%), while in HDS nickel phosphide had very high conversion (90% vs. 77%).

The overall activity of the phosphides was superior to or comparable to that of the sulfide. Also very attractive was the fact that the phosphides showed lower hydrogenation activity than the sulfide, indicating a more effective use of hydrogen, and no cracking.

The phosphides were tested for 100 hours and again did not display deactivation. Analysis of the products by XRD after reaction revealed that there was no change in bulk crystal structure (Figure 9). Furthermore, XPS revealed that only about 2 mol% of sulfur

accumulated on the surface of the catalysts after reaction for 100 hours. These results again demonstrate that the catalysts are completely stable in a sulfur environment.

Example 11

A pressing problem in hydrotreating is the removal of sulfur from refractory compounds like alkyl substituted dibenzothiophenes. This is the problem of deep HDS. In this example the conditions were the same as in Example 7 except that the feed contained 4,6-dimethyldibenzothiophene (500 ppm S), quinoline (200 ppm N), and the solvent was hexadecane. The phosphide catalysts tested were $\text{Ni}_2\text{P}/\text{SiO}_2$ and $\text{NiMoP}_2/\text{SiO}_2$. Comparison was made to a highly optimized commercial Ni-Mo-S/ Al_2O_3 catalyst (Criterion 424) which was sulfided *in situ* at 400 °C in 10% $\text{H}_2\text{S}/\text{H}_2$ before use. The conversions obtained in HDS are shown in Figure 10. The comparison is on the basis of 70 μmol of active sites loaded in the reactor. The sites were titrated by CO chemisorption for the phosphides and low temperature O_2 chemisorption for the sulfide. As shown in Figure 10, the Ni_2P catalyst has higher activity than the commercial catalyst.

It will be readily understood by those persons skilled in the art that the present invention is susceptible to broad utility and application. Many embodiments and adaptations of the present invention other than those herein described, as well as many variations, modifications and equivalent arrangements, will be apparent from or reasonably suggested by the present invention and the foregoing description without departing from the substance or scope of the present invention.

Accordingly, while the present invention has been described in detail in relation to its preferred embodiment, it is to be understood that this disclosure is only illustrative and exemplary of the present invention and is made merely for purposes of providing a

full and enabling disclosure of the invention. The foregoing disclosure is not intended to be construed to limit the present invention or otherwise exclude any other embodiments, adaptations, variations, modifications or equivalent arrangements, the present invention being limited only by the claims and the equivalents thereof.

CLAIMS

What is claimed is:

1. A catalyst comprising:

a metal phosphide complex having the formula MP_x , wherein M is selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, and wherein x ranges from about 0.1 to about 10; and

a high surface area support, wherein the metal phosphide complex is dispersed on the high surface area support.

2. The catalyst of claim 1 wherein the high surface area support is selected from the group consisting of carbon, silica, alumina, titania, thoria, magnesia, zirconia, kaolin, bentonite, kieselguhr, zeolites, and combinations thereof.

3. The catalyst of claim 1 further comprising a promoter selected from the group consisting of the alkali metals, alkaline earth metals, platinum group metals, rhenium, copper, halides, boron, carbon, nitrogen, aluminum, sulfur, gallium germanium, arsenic, tin, antimony, bismuth, selenium and tellurium.

4. The catalyst of claim 1 wherein x ranges from about 0.5 to about 3.

5. The catalyst of claim 1 wherein the metal phosphide complex is deposited on the support in the range of about 1 to about 40% by weight complex to support.

6. The catalyst of claim 1 wherein the metal phosphide complex is deposited on the support in the range of about 10 to about 30% by weight complex to support.

7. A metal phosphide catalyst comprising:

5 a metal phosphide complex having the formula $A_aB_bP_y$, wherein A and B are each selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, wherein the sum of a and b is 1, the ratio of a to b ranges from about 0.01 to about 100, and y ranges from about 0.1 to about 10; and

a high surface area support, wherein the metal phosphide complex is dispersed on
10 the high surface area support.

8. The metal phosphide catalyst of claim 7 wherein the high surface area support is selected from the group consisting of carbon, silica, alumina, titania, thoria, magnesia, zirconia, kaolin, bentonite, kieselguhr, zeolites, and combinations thereof.

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9. The catalyst of claim 7 further comprising a promoter selected from the group consisting of the alkali metals, alkaline earth metals, platinum group metals, rhenium, copper, halides, boron, carbon, nitrogen, aluminum, sulfur, gallium germanium, arsenic, tin, antimony, bismuth, selenium and tellurium.

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10. The catalyst of claim 7 wherein the ratio of a to b ranges from about 0.1 to about 10.

11. The catalyst of claim 7 wherein the ratio of a to b ranges from about 0.2 to about 5 and wherein y ranges from about 0.5 to about 3.

12. The catalyst of claim 7 wherein the metal phosphide complex is deposited on the support in the range of about 1 to about 40% by weight complex to support.

13. The catalyst of claim 7 wherein the metal phosphide complex is deposited on the support in the range of about 10 to about 30% by weight complex to support.

10 14. A method for hydrotreating a hydrocarbon feed comprising the step of:
exposing the hydrocarbon feed to a catalyst in an atmosphere containing
hydrogen, wherein the catalyst comprises:
at least one metal selected from the group consisting of V, Cr, Mn, Fe, Co, Ni,
Nb, Mo, Ta, and W, wherein at least a portion of said at least one metal is in the form of a
15 phosphide; and
a high surface area support, wherein the metal phosphide complex is dispersed on
the high surface area support.

15. The method of claim 14 wherein the phosphide has the formula MP_x , wherein M
20 is selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, and
wherein x ranges from about 0.1 to about 10.

16. The method of claim 15 wherein x ranges from about 0.5 to about 3.

17. The method of claim 14 wherein the phosphide has the formula $A_aB_bP_y$, wherein A and B are each selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, wherein the sum of a and b is 1, the ratio of a to b ranges from about 0.01 to about 100, and y ranges from about 0.1 to about 10
18. The method of claim 17 wherein the ratio of a to b ranges from about 0.1 to about 10.
19. The method of claim 17 wherein the ratio of a to b ranges from about 0.2 to about 5 and wherein y ranges from about 0.5 to about 3.
20. The method of claim 14 wherein the step of exposing the hydrocarbon feed to a catalyst is sufficient to remove nitrogen from the hydrocarbon feed.
21. The method of claim 14 wherein the step of exposing the hydrocarbon feed to a catalyst is sufficient to remove oxygen from the hydrocarbon feed.
22. The method of claim 14 wherein the step of exposing the hydrocarbon feed to a catalyst is sufficient to hydrogenate an unsaturated organic compound in the hydrocarbon feed.

23. The method of claim 14 wherein the step of exposing the hydrocarbon feed to a catalyst is sufficient to hydroisomerize an organic compound in the hydrocarbon feed.

24. The method of claim 14 wherein the high surface area support is selected from the group consisting of carbon, silica, alumina, titania, thoria, magnesia, zirconia, kaolin, bentonite, kieselguhr, zeolites, and combinations thereof.

25. The method of claim 14 wherein the hydrocarbon feed is selected from the group consisting of middle distillates, kero, naptha, gas oil obtained by catalytic cracking, gas oil obtained by thermal cracking, straight-run gas oil, coker gas oil, vacuum gas oils, heavy gas oils, coal liquids, feeds extracted from tar sands, and feeds extracted from shale.

26. The method of claim 14 further comprising the step of processing the hydrocarbon feed in the presence of the catalyst at a temperature ranging from about 250 to about 450 °C, pressure ranging from about 5 to about 250 bar, space velocities ranging from about 0.1 to about 10 hr⁻¹, and H₂/feed ratios ranging from about 1000 to about 15000 scf/barrel.

27. The method of claim 14 wherein the metal phosphide complex is deposited on the support in the range of about 1 to about 40% by weight complex to support.

28. The catalyst of claim 14 wherein the metal phosphide complex is deposited on the support in the range of about 10 to about 30% by weight complex to support.

29. A metal catalyst comprising:

5 at least one metal selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, wherein at least a portion of said at least one metal is in the form of a phosphide; and

a high surface area support wherein the said at least one metal and said phosphide is dispersed on said high surface area support.

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30. The catalyst of claim 29 wherein the high surface area support is selected from the group consisting of carbon, silica, alumina, titania, thoria, magnesia, zirconia, kaolin, bentonite, kieselguhr, zeolites, and combinations thereof.

15 31. The catalyst of claim 29 further comprising a promoter selected from the group consisting of the alkali metals, alkaline earth metals, platinum group metals, rhenium, copper, halides, boron, carbon, nitrogen, aluminum, sulfur, gallium germanium, arsenic, tin, antimony, bismuth, selenium and tellurium.

20 32. The catalyst of claim 29 wherein the metal phosphide complex is deposited on the support in the range of about 1 to about 40% by weight complex to support.

33. The catalyst of claim 29 wherein the metal phosphide complex is deposited on the support in the range of about 10 to about 30% by weight complex to support.

34. A process for hydrodesulfurizing a hydrocarbon feed containing sulfur

5 compounds comprising the step of:

exposing the hydrocarbon feed to a catalyst, wherein the catalyst comprises:

at least one metal selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, wherein at least a portion of said at least one metal is in the form of a phosphide; and

10 a high surface area support, wherein the metal phosphide complex is dispersed on the high surface area support.

35. The method of claim 34 wherein the phosphide has the formula MP_x , wherein M is selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, and

15 wherein x ranges from about 0.1 to about 10.

36. The method of claim 35 wherein x ranges from about 0.5 to about 3.

37. The method of claim 34 wherein the phosphide has the formula $A_aB_bP_y$, wherein

20 A and B are each selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, wherein the sum of a and b is 1, the ratio of a to b ranges from about 0.01 to about 100, and y ranges from about 0.1 to about 10

38. The method of claim 37 wherein the ratio of a to b ranges from about 0.1 to about 10.

39. The method of claim 37 wherein the ratio of a to b ranges from about 0.2 to about 5 and wherein y ranges from about 0.5 to about 3.

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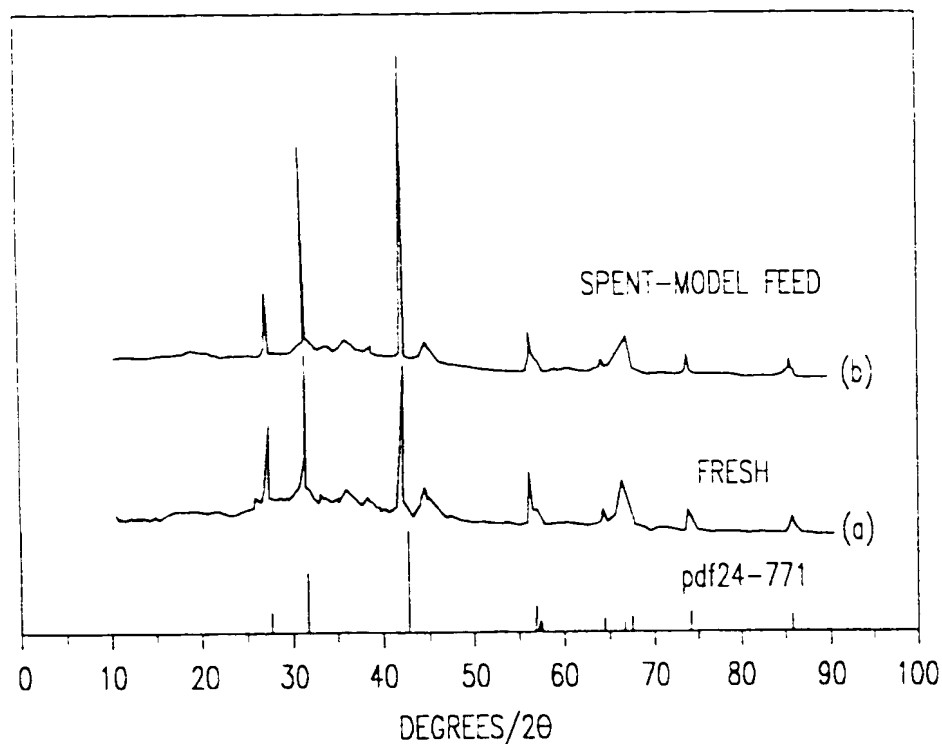


FIG. 1

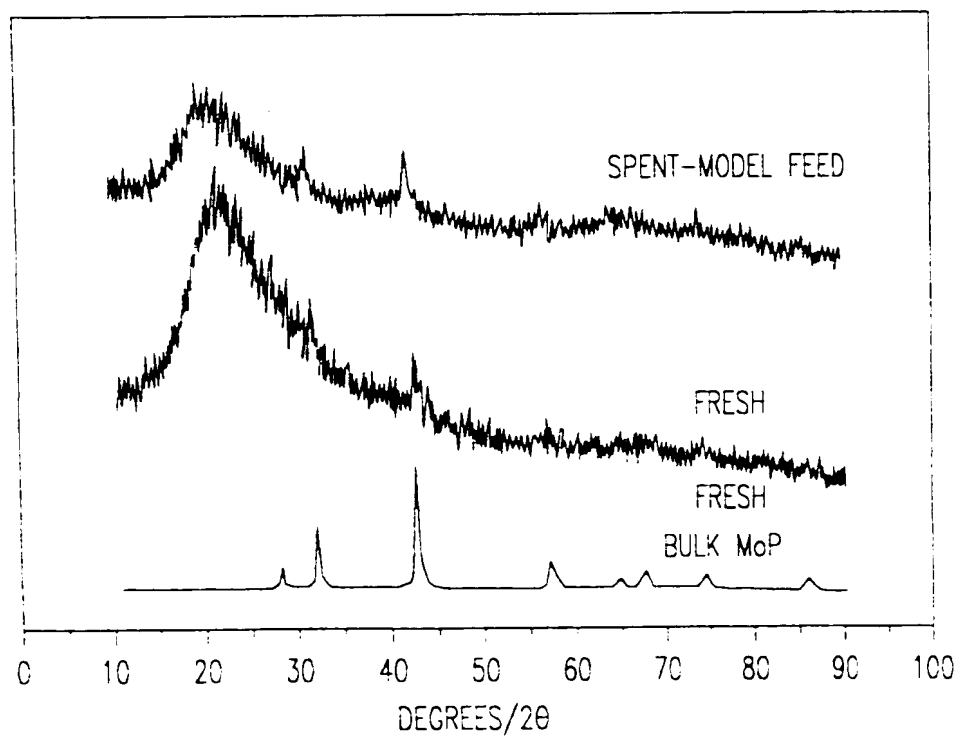


FIG. 2

SUBSTITUTE SHEET (RULE 26)

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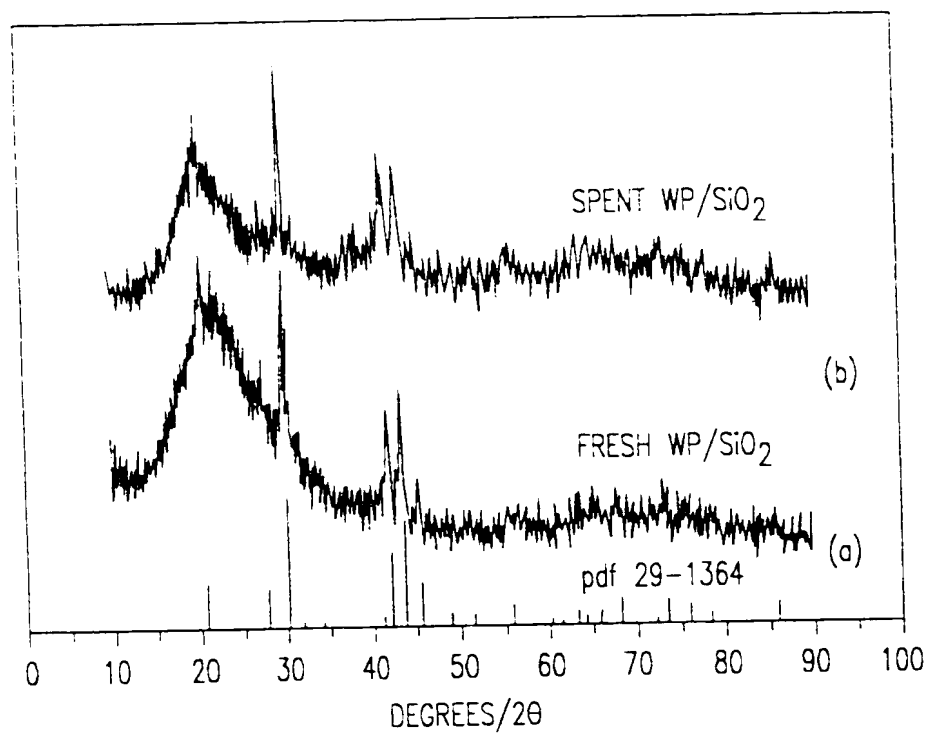


FIG. 3

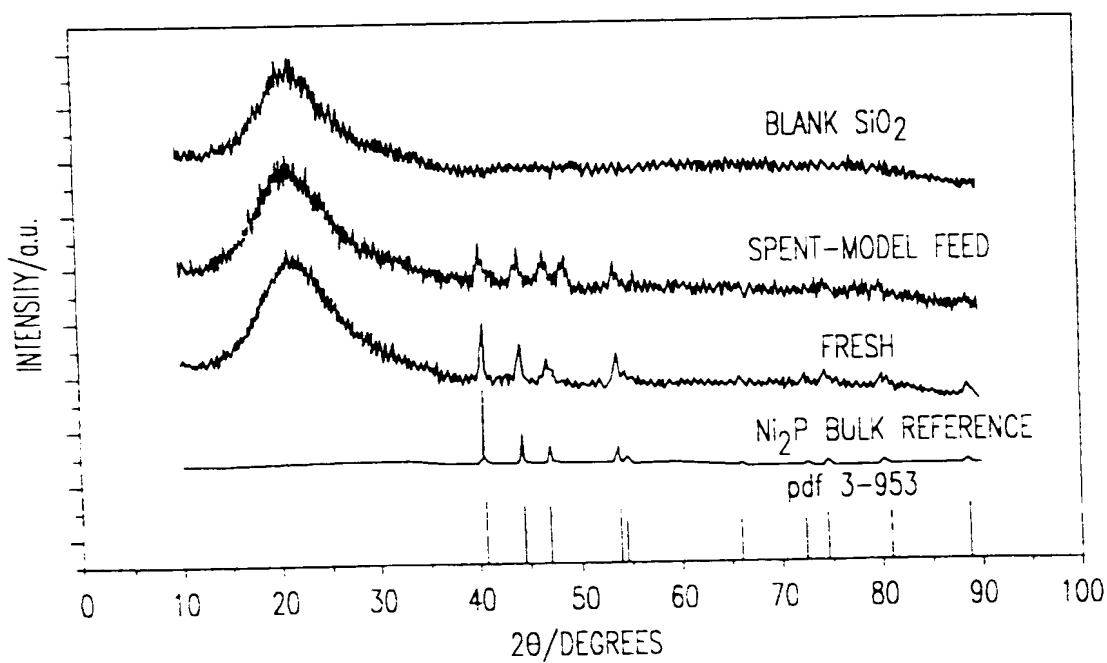


FIG. 4

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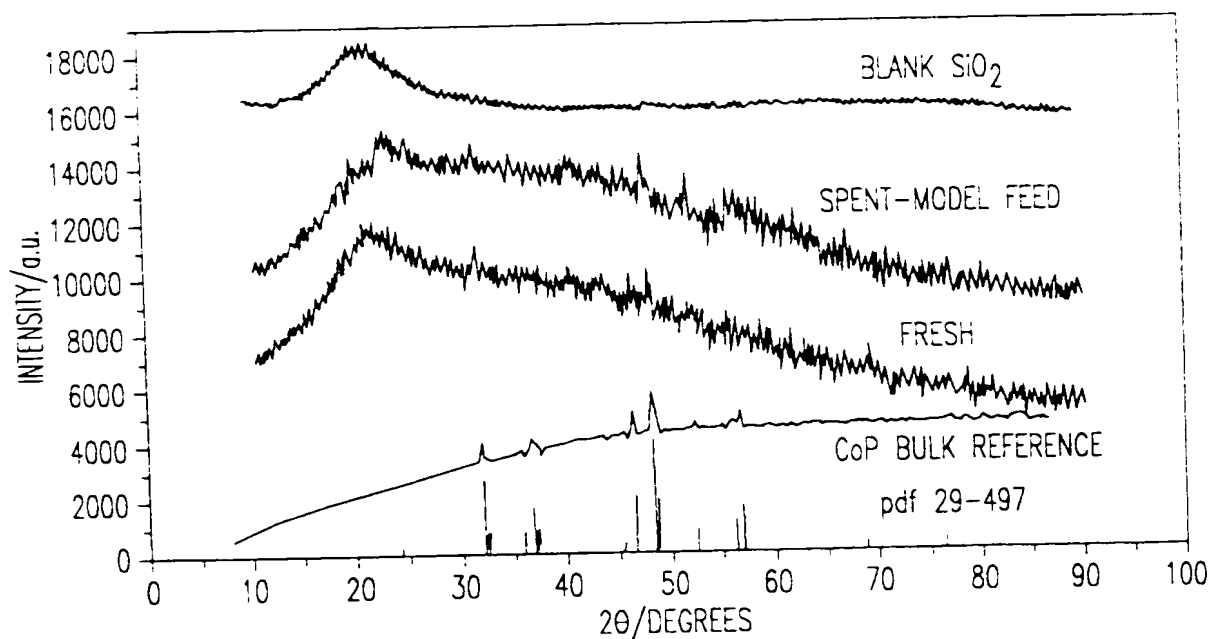


FIG. 5

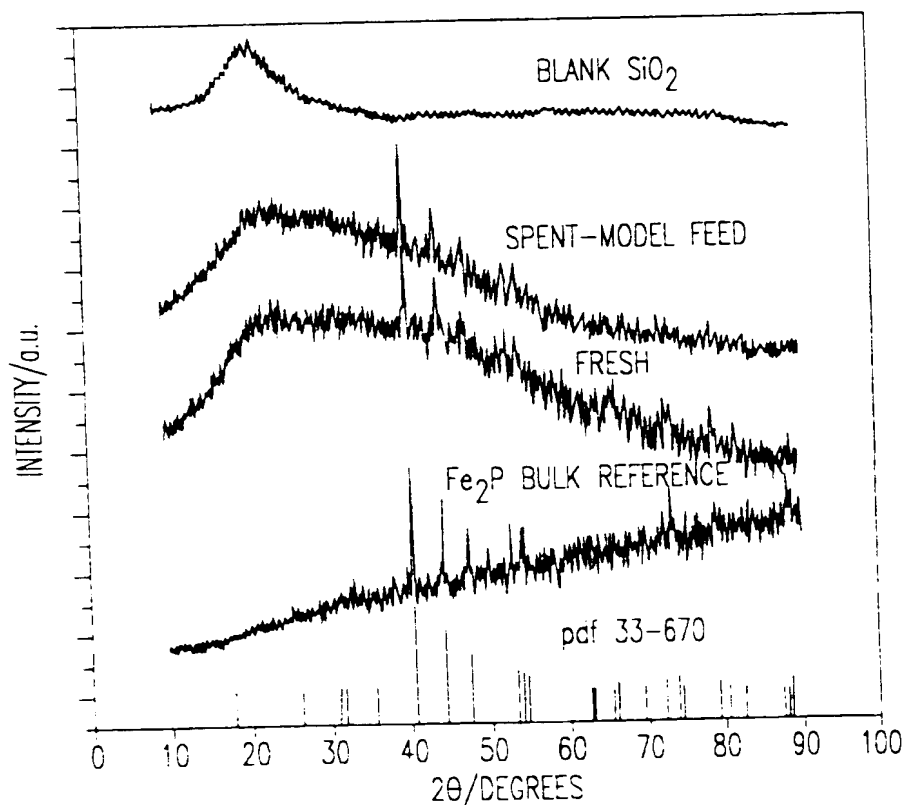


FIG. 6

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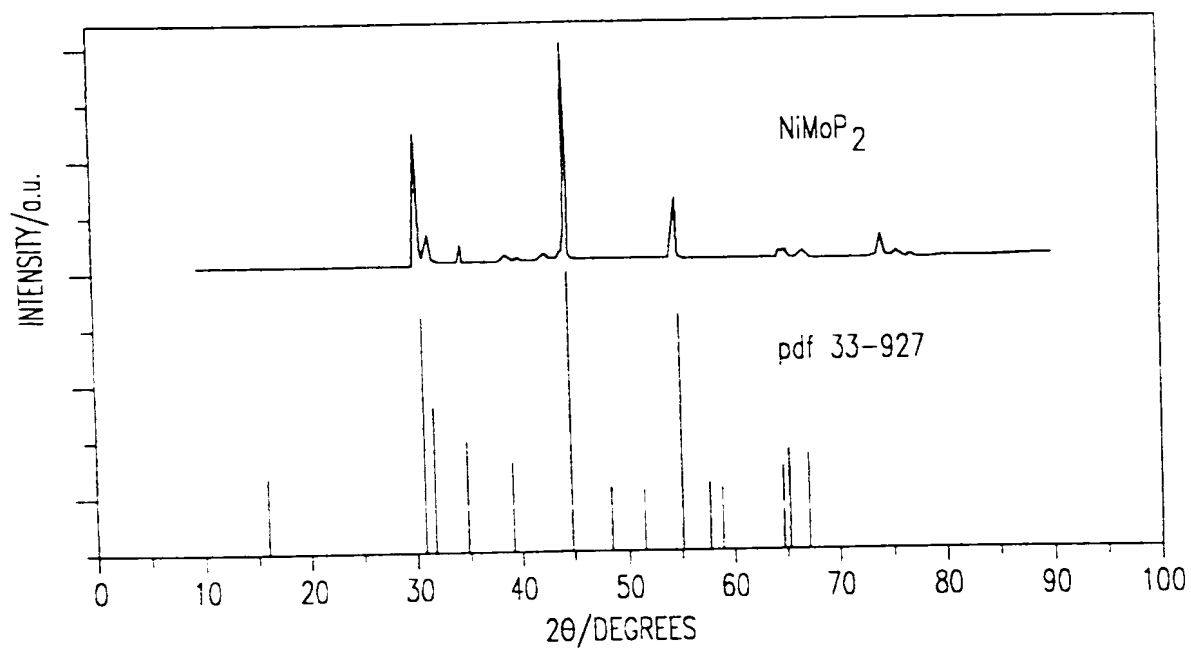


FIG. 7

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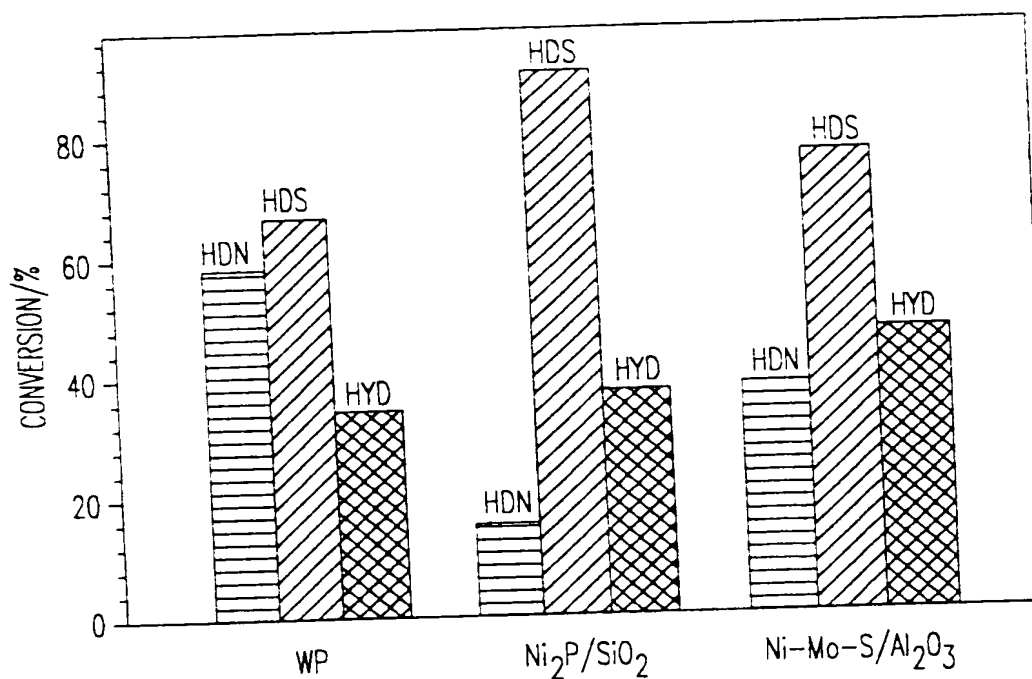


FIG. 8

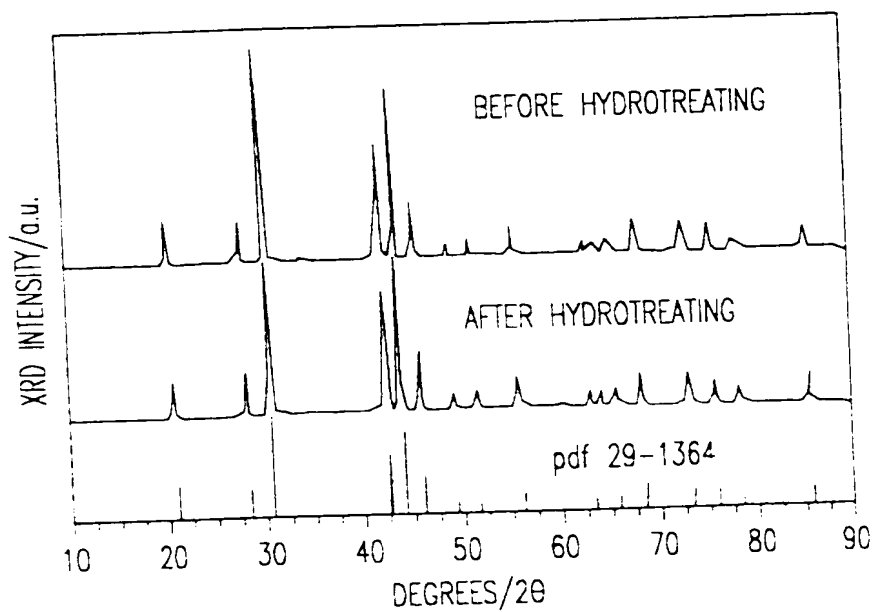


FIG. 9

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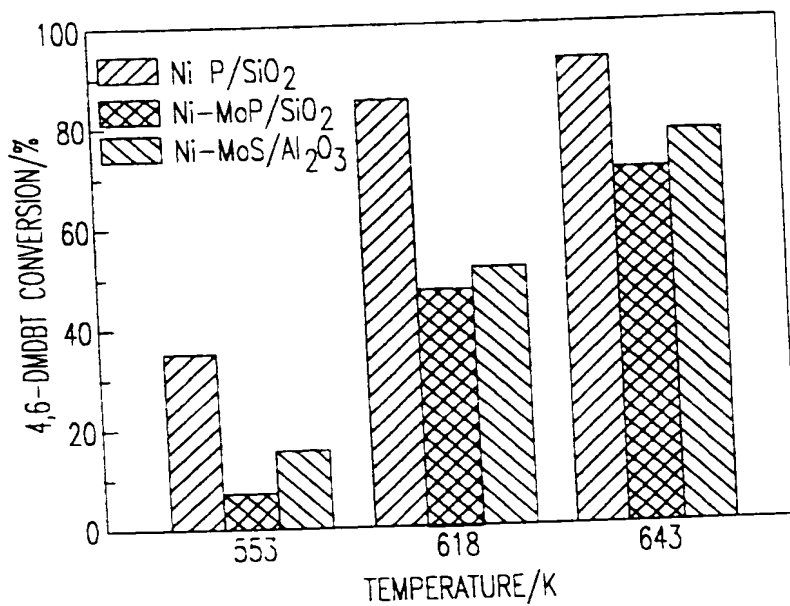


FIG. 10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/26603

A. CLASSIFICATION OF SUBJECT MATTER

IPC(*) Please See Extra Sheet

US CL Please See Extra Sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. Please See Extra Sheet

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,367,137 A (ANTOS ET AL.) 04 JANUARY 1983, SEE PARTICULARLY COLUMN 1, LINES 41-44, COLUMN 4, LINE 54-COLUMN 7, LINE 43 AND COLUMN 14, LINE 27-COLUMN 5, LINE 25.	1-39
X - Y	US 4,454,246 A (FUNG) 12 JUNE 1984, SEE PARTICULARLY COLUMN 3, LINE 16-COLUMN 4, LINE 43.	1-33 ---- 1-33
X - Y	US 4,359,406 A (FUNG) 16 NOVEMBER 1982, SEE PARTICULARLY COLUMN 3, LINE 16-COLUMN 4, LINE 43.	1-33 ---- 1-33

☐

Further documents are listed in the continuation of Box C.

☐

See patent family annex.

* Special categories of cited documents	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"I" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

01 NOVEMBER 2000

Date of mailing of the international search report

12 JAN 2001

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/26603

A. CLASSIFICATION OF SUBJECT MATTER
IPC (C)

C10G 45/04; B01J 21/02, 21/04, 21/06, 21/08, 21/10, 21/16, 21/18, 27/02, 27/045, 27/08, 27/14, 27/182, 27/185, 27/186,
27/188, 27/19, 27/192, 27/195, 27/198, 27/199

A. CLASSIFICATION OF SUBJECT MATTER
US CL

502.60, 74, 77, 78, 79, 80, 174, 180, 181, 182, 183, 184, 185, 200, 202, 204, 205, 206, 207, 208, 209, 210, 211, 212,
213, 208.143, 216R, 217, 254H

B. FIELDS SEARCHED

Minimum documentation searched

Classification System: U.S.

502.60, 74, 77, 78, 79, 80, 174, 180, 181, 182, 183, 184, 185, 200, 202, 204, 205, 206, 207, 208, 209, 210, 211, 212,
213, 208.143, 216R, 217, 254H